

## CD221. LECTURE 10. LEGENDRE TRANSFORMS IN THERMODYNAMICS

The method of Legendre transforms gives us a way to construct new (and equivalent) forms of a fundamental relation in which the independent variables can be intensive parameters. For instance, consider a system defined by the fundamental relation

$$U = U(S, V, N) \quad (1)$$

Let's carry out a series of partial Legendre transforms of  $U$  with respect to one or more of the variables  $S$ ,  $V$  and  $N$ .

### 1. Legendre transform of $U$ with respect to $S$ .

By definition, this transform is the function

$$\begin{aligned} U[T] &\equiv U - \left( \frac{\partial U}{\partial S} \right)_{V,N} S \\ &= U - TS \end{aligned} \quad (2)$$

It is given the special symbol  $F$  (so  $F = U - TS$ ), and is referred to as the Helmholtz potential.  $F$  becomes solely a function of  $T$ ,  $V$  and  $N$  once  $U$  and  $S$  are eliminated from Eq. (2) using Eq. (1) and the definition of  $T$  as the slope  $(\partial U / \partial S)_{V,N}$ . In other words,

$$F = F(T, V, N) \quad (3)$$

and this is a fundamental relation.

### 2. Legendre transform of $U$ with respect to $V$ .

By definition, this transform is the function

$$\begin{aligned} U[P] &\equiv U - \left( \frac{\partial U}{\partial V} \right)_{S,N} V \\ &= U + PV \end{aligned} \quad (4)$$

It is given the special symbol  $H$  (so  $H = U + PV$ ) and is referred to as the enthalpy.  $H$  becomes solely a function of  $S$ ,  $P$  and  $N$  once  $U$  and  $V$  are eliminated from Eq. (4) using Eq. (1) and the definition of  $-P$  as the slope  $(\partial U / \partial V)_{S,N}$ . In other words,

$$H = H(S, P, N) \quad (5)$$

and this is a fundamental relation.

### 3. Legendre transform of $U$ with respect to $S$ and $V$ .

By definition, this transform is the function

$$\begin{aligned} U[T, P] &\equiv U - \left( \frac{\partial U}{\partial S} \right)_{V, N} S - \left( \frac{\partial U}{\partial V} \right)_{S, N} V \\ &= U - TS + PV \end{aligned} \quad (6)$$

It is given the special symbol  $G$  (so  $G = U - TS + PV$ ) and is referred to as the Gibbs potential.  $G$  becomes solely a function of  $T$ ,  $P$  and  $N$  once  $U$ ,  $S$  and  $V$  are eliminated from Eq. (6) using Eq. (1) and the definition of  $T$  as the slope  $(\partial U / \partial S)_{V, N}$  and  $-P$  as the slope  $(\partial U / \partial V)_{S, N}$ . In other words,

$$G = G(T, P, N) \quad (7)$$

and this is a fundamental relation.

### 4. Legendre transform of $U$ with respect to $S$ and $N$ .

By definition, this transform is the function

$$\begin{aligned} U[T, \mu] &\equiv U - \left( \frac{\partial U}{\partial S} \right)_{V, N} S - \left( \frac{\partial U}{\partial N} \right)_{S, V} N \\ &= U - TS - \mu N \end{aligned} \quad (8)$$

It is given the special symbol  $\Psi$  (so  $\Psi = U - TS - \mu N$ ) and is referred to as the grand potential.  $\Psi$  becomes solely a function of  $T$ ,  $V$  and  $\mu$  once  $U$ ,  $S$  and  $N$  are eliminated from Eq. (8) using Eq. (1) and the definition of  $T$  as the slope  $(\partial U / \partial S)_{V, N}$  and  $\mu$  as the slope  $(\partial U / \partial N)_{S, V}$ . In other words,

$$\Psi = \Psi(T, V, \mu) \quad (9)$$

and this is a fundamental relation.

#### • The thermodynamic potentials in differential form

The differential forms of the above thermodynamic potentials (i.e., the expressions for the infinitesimal changes to  $F$ ,  $H$ ,  $G$  and  $\Psi$  following infinitesimal changes to the

variables they depend on) are easily derived. As an example consider  $F$ , defined as  $F = U - TS$ . Its first differential is, by definition

$$dF = dU - d(TS) = dU - TdS - SdT \quad (10)$$

We already know the differential form of  $U$ ; it is

$$dU = TdS - PdV + \mu dN \quad (11)$$

Substitution of Eq. (11) into Eq. (10) leads to the desired expression:

$$dF = -SdT - PdV + \mu dN \quad (12)$$

The differential forms of the other potentials are derived in the same way; they are

$$dH = TdS + VdP + \mu dN \quad (13)$$

$$dG = -SdT + VdP + \mu dN \quad (14)$$

$$d\Psi = -SdT - PdV - Nd\mu \quad (15)$$

• Thermodynamic potentials and their natural variables

The variables on which the thermodynamic potentials  $F$ ,  $H$ ,  $G$  and  $\Psi$  depend when the potential is constructed as the Legendre transform of the fundamental relation in the energy representation are called the potentials' natural variables. We thus have the following table:

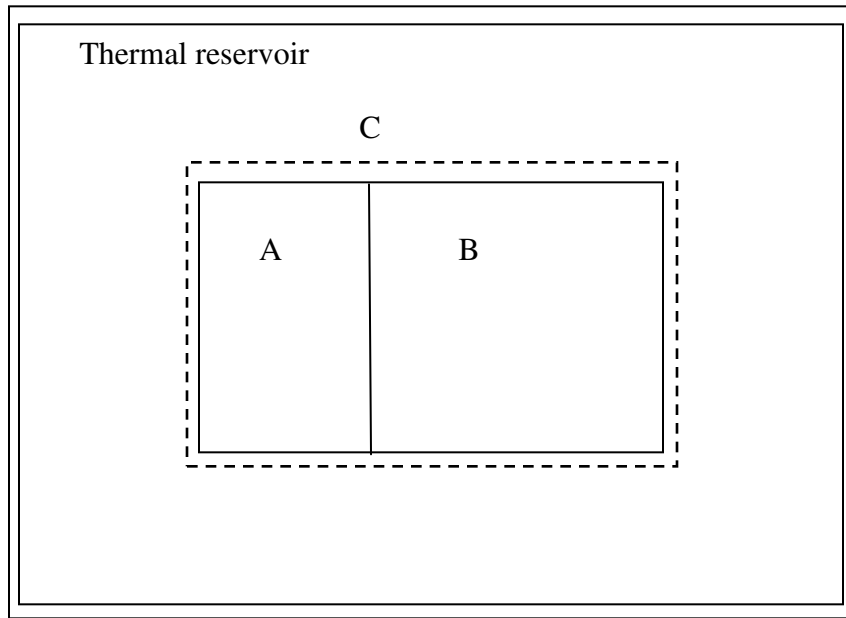
| <u>Thermodynamic Potential</u> | <u>Natural Variables</u> |
|--------------------------------|--------------------------|
| $U$                            | $S, V, N$                |
| $F$                            | $T, V, N$                |
| $H$                            | $S, P, N$                |
| $G$                            | $T, P, N$                |
| $\Psi$                         | $T, V, \mu$              |

( $U$  can also be regarded as a thermodynamic potential.) It's important to note that it is only when these thermodynamic potentials are expressed in terms of their corresponding natural variables that they become fundamental relations. If for instance  $G$  were written as a function of, say,  $T$ ,  $V$  and  $N$  instead of  $T$ ,  $P$  and  $N$ , that relation would then not be a fundamental relation. When a thermodynamic potential is expressed in terms of its natural variables, all thermodynamic information can be obtained from it purely by taking derivatives.

- Extremum principles for the thermodynamic potentials

We've seen that in the approach to equilibrium, a system will maximize its entropy at constant energy, or minimize its energy at constant entropy. What happens to the other thermodynamic potentials –  $F$ ,  $H$ ,  $G$  and  $\Psi$  – during a change of state?

Take the case of  $F$  as an example. To understand how it behaves as systems equilibrate, consider a composite system (called  $C$  for short) made up of two sub-systems  $A$  and  $B$ . Let's suppose that  $C$  is at some fixed temperature  $T$ . To achieve this condition  $C$  is placed in diathermal contact with a heat bath (also called a thermal reservoir), which is a system that by definition exchanges only heat with its surroundings and which is so large that no matter how much heat flows into or out of it, its temperature remains the same. We'll further suppose that  $C$  and the thermal reservoir together constitute a closed (i.e., isolated) system. The arrangement is shown schematically below:



When the internal constraint is now released (under conditions of constant  $T$ )  $C$  evolves to some new equilibrium state. If  $U$  denotes the energy of  $C$  and  $U_R$  that of the reservoir, this equilibrium state minimizes the total energy at fixed total entropy. Therefore,

$$d(U + U_R) = 0 \quad (16)$$

Furthermore, because the total entropy is assumed fixed, we have

$$d(S + S_R) = 0 \quad (17)$$

Also, since the energy change of the reservoir is solely due to heat exchange, it follows that

$$dU_R = T_R dS_R \quad (18)$$

Substituting Eq. (18) into Eq. (16),

$$dU + T_R dS_R = 0 \quad (19)$$

But from Eq. (17),  $dS = -dS_R$ , so Eq. (19) becomes

$$dU - T_R dS = 0 \quad (20)$$

At the same time, since  $T_R = T$ , Eq. (20) is reduced to

$$dU - T dS = 0$$

or

$$d(U - TS) = 0 \quad (21)$$

(since  $T$  is a constant.) But by the definition of  $F$ , Eq. (21) implies that

$$dF = 0 \quad (22)$$

So after removal of the internal constraint, the Helmholtz potential of C is at an extremum. To determine whether this extremum is a minimum or a maximum, we note that the total energy of C and the reservoir is at a minimum, and that therefore

$$d^2(U + U_R) > 0 \quad (23)$$

Eq. (23) can be rewritten as

$$d^2U + d^2U_R > 0$$

or as

$$d^2U + d(dU_R) > 0 \quad (24)$$

(A second differential can be thought of as the first differential of a first differential.) But  $dU_R = T_R dS_R = -T dS$ , so Eq. (24) becomes

$$d^2U - d(T dS) > 0$$

which is the same as

$$d^2U - Td^2S > 0$$

(since  $T$  is a constant), which in turn is equal to

$$d^2(U - TS) > 0$$

So we're finally left with

$$d^2F > 0 \tag{25}$$

which means that  $F$  is at a minimum at equilibrium.

We can embody this result in the following general principle: **The equilibrium value of any unconstrained internal parameter in a system in diathermal contact with a thermal reservoir minimizes the Helmholtz potential over the manifold of states for which  $T = T_R$ .**

The same line of reasoning is easily extended to a composite system  $C$  that is maintained at constant pressure  $P$  through contact with a “pressure reservoir”, such that  $C$  and the reservoir constitute another composite system that is closed. This then leads to the following principle: **The equilibrium value of any unconstrained internal parameter in a system in contact with a pressure reservoir minimizes the enthalpy  $H$  over the manifold of states of constant pressure  $P = P_R$ .**

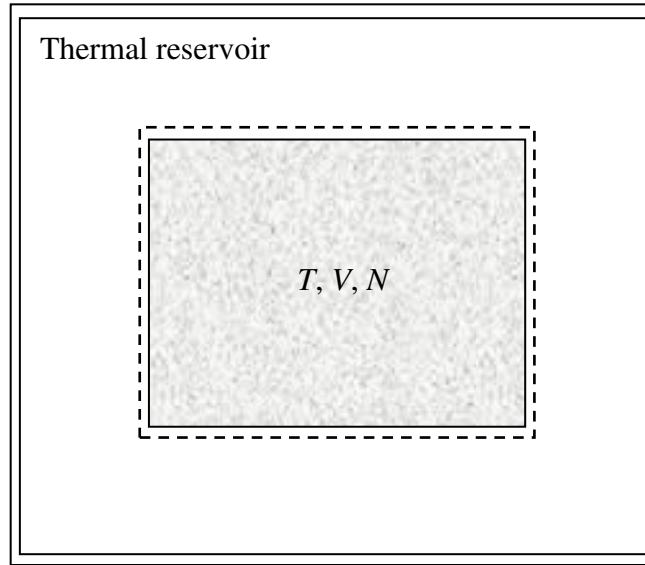
A similar analysis of a composite system  $C$  maintained at constant  $T$  and  $P$  through contact with a temperature *and* pressure reservoir yields this principle: **The equilibrium value of any unconstrained internal parameter in a system in contact with a temperature and pressure reservoir minimizes the Gibbs potential  $G$  over the manifold of states of constant temperature  $T = T_R$  and constant pressure  $P = P_R$ .**

And finally, for a composite system  $C$  maintained at constant  $T$  and  $\mu$  through contact with a temperature and matter reservoir, it similarly follows that: **The equilibrium value of any unconstrained internal parameter in a system in contact with a temperature and matter reservoir minimizes the grand potential  $\Psi$  over the manifold of states of constant temperature  $T = T_R$  and constant chemical potential  $\mu = \mu_R$ .**

#### • Microscopic Connection

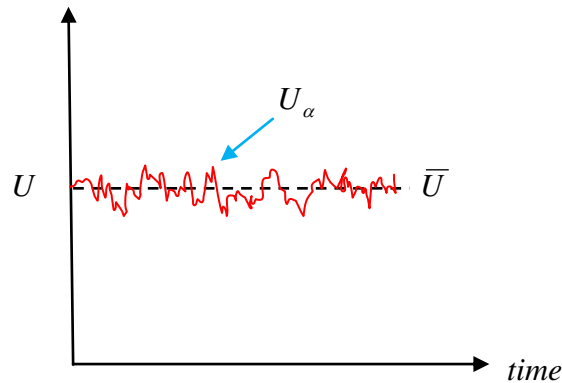
We're now in a position to address the following problem: given some system whose macroscopic characterization requires the specification of one or more *intensive* parameters, how are its thermodynamic properties derived from a knowledge of just the microscopic properties of its constituent elements?

To answer this question, consider, as a specific example, a system of fixed volume  $V$ , a fixed number of particles  $N$ , and a constant temperature  $T$ , the temperature being maintained constant through thermal contact with a heat bath. The set-up is as shown below:



We'll assume that the system and reservoir together constitute a composite system that's closed. Denote the energy, the volume and the number of particles of this closed composite system as  $U_0, V_0$  and  $N_0$ , respectively. Similarly, denote the corresponding variables of the reservoir by  $U_R, V_R$  and  $N_R$  and those of the system by  $U, V$  and  $N$ .

Because the wall between the system and reservoir is diathermal, energy continuously flows into and out of the system, maintaining its temperature at  $T$ , the temperature of the reservoir. The energy of the system therefore fluctuates, as in the figure below



At any one instant of time, the system will be found in one of the microstates that is compatible with the energy the system has at that particular time. As the energy of the system fluctuates, so also does that of the reservoir, but without violating the constraint that the total energy of system and reservoir always equal  $U_0$ . Over the course of a thermodynamic measurement, however, which corresponds to long timescales, the energy fluctuations of the system average out to some constant time-independent value  $\bar{U}$ .

Suppose that at some instant of time, the system is in a definite microstate  $\alpha$ , in which its energy is  $U_\alpha$  (as illustrated in the figure.) If the system were an ideal gas, for instance,  $\alpha$  would be the label or serial number of the state in which particle 1 was in a definite energy state, particle 2 was in a definite energy state, and so on, for all the other particles. In general, because the reservoir is so much bigger than the system of interest, it is the case that

$$U_\alpha \ll U_R \quad \forall \alpha \quad (26)$$

Now when the system is in the microstate  $\alpha$  corresponding to a macrostate with energy  $U_\alpha$ , the reservoir will have an energy  $U_0 - U_\alpha$  (by energy conservation) that we'll denote  $U_{R\alpha}$ , i.e.,  $U_{R\alpha} = U_0 - U_\alpha$ . There will be many possible microstates of the reservoir that have this energy, and if the number of such microstates is denoted  $\Omega_{R\alpha}$ , then

$$\Omega_{R\alpha} = \Omega_R(U_{R\alpha}) = \Omega_R(U_0 - U_\alpha) \quad (27)$$

(In general,  $\Omega_{R\alpha}$  will also be a function of the volume and number of particles, but these are fixed, so we needn't account for them explicitly.) If the reservoir can be in one of  $\Omega_{R\alpha}$  microstates when the system is in microstate  $\alpha$ , we can determine the number of possible microstates available to the composite system as a whole. If that number is denoted  $\Omega_{0\alpha}$ , it must be given by

$$\begin{aligned} \Omega_{0\alpha} &= \Omega_{R\alpha} \times 1 \\ &= \Omega_{R\alpha} \end{aligned} \quad (28)$$

(The factor of 1 describes the fact that there is just one microstate labelled  $\alpha$ .) The *total* number of microstates of the composite system (with energy  $U_0$ ) is a larger number; let's denote it  $\Omega_0$ . Of these  $\Omega_0$  microstates of the composite system (all equally likely),  $\Omega_{0\alpha}$  ( $= \Omega_{R\alpha}$ ) of them correspond to the system being in microstate  $\alpha$ . So the probability of the system finding itself in  $\alpha$  (call it  $p_\alpha$ ) is the number of ways this can happen ( $\Omega_{R\alpha}$ ) divided by the number of ways anything can happen ( $\Omega_0$ ). That is,



$$p_\alpha = \frac{\Omega_{R\alpha}}{\Omega_0} \quad (29)$$

This identification has important implications. It means, in particular, that the microstates of a system at constant  $T$  aren't all equally probable, as they were in a system at constant  $U$ . The probability of a microstate  $\alpha$  in a constant temperature system depends on its energy – the more energy there is in the system, the less there is in the reservoir, the smaller therefore is the corresponding number of reservoir microstates, and the smaller accordingly is the probability of microstate  $\alpha$ .

It's now possible to connect these results to thermodynamics. This is how we proceed. Let  $S_{R\alpha}$  denote the entropy of the reservoir when the system is in  $\alpha$ . The Boltzmann equation tells us that

$$S_{R\alpha} = k_B \ln \Omega_{R\alpha} \quad (30)$$

which can be rearranged to

$$\Omega_{R\alpha} = \exp(S_{R\alpha} / k_B). \quad (31)$$

$S_{R\alpha}$  in these relations depends on the amount of energy the reservoir has when the system is in  $\alpha$ , which is  $U_0 - U_\alpha$ . If this dependence is shown explicitly, Eq. (31) becomes

$$\Omega_{R\alpha} = \exp \left[ \frac{1}{k_B} S_R(U_0 - U_\alpha) \right] \quad (32)$$

a result that also follows from Eq. (27). Since we've assumed that  $U_\alpha$  is much less than the energy of the reservoir, it's possible to approximate the entropy in Eq. (32) by a Taylor expansion around  $U_0$ . This expansion takes the form

$$S_R(U_0 - U_\alpha) \approx S_R(U_0) - \frac{\partial S_R}{\partial U_R} U_\alpha + \dots \quad (33)$$

The partial derivative in Eq. (33) is nothing but the reciprocal of the temperature of the reservoir  $T$ , and so,

$$S_R(U_0 - U_\alpha) \approx S_R(U_0) - \frac{U_\alpha}{T} + \dots \quad (34)$$

Substituting Eq. (34) back into Eq. (32), we get

$$\Omega_{R\alpha} = \exp[S_R(U_0)/k_B - U_\alpha/k_B T] \quad (35)$$

The quantity  $S_R(U_0)$  is the entropy the reservoir would have had if it contained all the energy  $U_0$  of the composite system, and is therefore some constant, independent of  $\alpha$ . Equation (35) can therefore be written as

$$\Omega_{R\alpha} = C_1 e^{-\beta U_\alpha} \quad (36)$$

where  $C_1$  is a constant, and  $\beta \equiv 1/k_B T$ . From the Boltzmann equation for the composite system as a whole, we also have the relation

$$\Omega_0 = e^{S_0/k_B} \quad (37)$$

If we substitute Eqs. (36) and (37) into Eq. (29), we arrive at an expression for the probability that the system is in  $\alpha$ :

$$p_\alpha = \frac{C_1 e^{-\beta U_\alpha}}{e^{S_0/k_B}} = C_2 e^{-\beta U_\alpha} \quad (38)$$

where the combination  $C_1/e^{S_0/k_B}$  is just another constant (viz.,  $C_2$ ) because  $S_0$  is a constant (the entropy of the composite system as a whole.) But  $C_2$  can actually be determined because we know that probabilities must add up to 1, so in Eq. (38), if we sum  $p_\alpha$  over all the possible microstates, the result will be 1, which means that

$$\sum_\alpha p_\alpha = 1 = C_2 \sum_\alpha e^{-\beta U_\alpha} \quad (39)$$

and so

$$C_2 = \frac{1}{\sum_\alpha e^{-\beta U_\alpha}} \quad (40)$$

The quantity  $\sum_\alpha e^{-\beta U_\alpha}$  is usually given the symbol  $Q$ , and it has a special name – the canonical partition function, sometimes also referred to as the sum over states. We'll see that it is the key quantity that connects to thermodynamics.

In terms of  $Q$ , the probability that the system is in some microstate  $\alpha$  is

$$p_\alpha = \frac{e^{-\beta U_\alpha}}{Q} = \frac{e^{-\beta U_\alpha}}{\sum_\alpha e^{-\beta U_\alpha}} \quad (41)$$

Contrast this expression with the expression for the probability of finding a system in  $\alpha$  when the energy (rather than the temperature) is fixed:  $p_\alpha = 1/\Omega$ .

We'll now find a way to relate Eq. (41) to a thermodynamic property of the system.